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Lewis acid catalyzed synthesis of di- and tri-saccharide sequences in O- and N-glycoproteins. The use of trimethylsilyltrifluoromethanesulfonate*

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Abstract

In the presence of trimethylsilyltrifluoromethanesulfonate as Lewis acid catalyst, β-acetates reacted, as glycosyl donors and with neighboring-group participation, with secondary hydroxyl groups of saccharides having low reactivity to give β-glycosidically linked di- and oligo-saccharides in high yields. The protecting groups of both compounds of the reaction had to be stable under acid conditions. Thus, the reaction of 1,2,3,4,6-penta-*O*-acetyl-β-D-galactopyranose with methyl 2-azido-4,6-di-*O*-benzoyl-2-deoxy-β-D-galactopyranoside gave, in 83% yield, methyl 2-azido-2,6-di-*O*-benzoyl-2-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-galactopyranoside which is a useful building unit. The glycosidic reactions under Lewis acid catalysis and Koenigs–Knorr conditions are compared. The efficiency of the Lewis acid-catalyzed procedure was demonstrated by the further synthesis of di- and tri-saccharides, such as lactosamine and chitobiose derivatives, whereby hydroxyl groups having low reactivity could be glycosylated in good yields.

* Communication LV in the series "Building Blocks of Oligosaccharides". Communication LIV, see bibliographic reference [1].

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Introduction

In addition to lactosamine, the disaccharide building block β-D-Galp-(1→3)-D-Gal-NAc is of great interest, since it occurs as a sequence in the majority of O-glycoproteins[2] and in gangliosides[3]. Compounds which contain this sequence as determinant are called T-antigen substances, exhibiting a corresponding immunological activity[4]. Whereas lactosamine is easily obtained from lactose and can be used to prepare a very effective synthesis building block[5-7], the analogous possibility of preparing a corresponding synthesis building block β-D-Galp-(1→3)-D-GalNAc does not exist. For the preparation of T-antigen structures and O-glycoproteins such a building block would be extremely useful. Previously we have had to prepare analogous structures by using a step-by-step synthesis[8-9].

For the synthesis of these building blocks with 2-azido-2-desoxy-D-galactose, it is necessary to form a β-(1→3)-glycosidic linkage with D-galactose. The use of 2-azido-2-desoxy-D-galactose is necessary since otherwise the α-glycosidic bond can be formed unselectively by the azide process[10,11], as in the bond formation with L-serine and L-threonine. However, the OH-3 group in 2-azido-2-desoxy-D-galactose only forms a weak β-glycosidic bond, as was reported in an earlier publication. Therefore, as is shown in the experiments detailed in this current paper, the attempt to achieve bonding of 2,3,4,6-tetra-O-acetyl-α-D-galactopyranosylbromide to this OH-3 group under Koenigs-Knorr conditions yields very unsatisfactory results. It was therefore necessary to use a fundamentally different method, and so we turned to the Lewis acid catalyzed glycoside synthesis.

Lewis acid catalyzed glycoside synthesis has been known for a long time; catalysts such as BF_3[12], $SnCl_4$[13] and $FeCl_3$[14] have been used. The utilization of β-acetates has proven especially advantageous. These react stereospecifically to produce β-gycosides due to the participation of neighbouring groups. To date, these reactions have been used predominantly only with simple alcohols or primary hydroxyl reactants. The only successful disaccharide syntheses involving a secondary hydroxyl group have been carried out using acetate as leaving group[14] with $FeCl_3$ catalyst, and using trichloroacetimidate

as leaving group[15] with BF_3 catalyst. In the present work we report the successful utilization of trimethylsilyltrifluoromethane sulfonic acid* (trimethylsilyltriflate) as Lewis acid catalyst. Trimethylsilyltriflate was used by VORBRÜGGEN[16] for the first time in nucleoside syntheses and by OGAWA et al[17] for the synthesis of glycosides from primary hydroxyl groups. Trimethylsilyltriflate has also proven useful in the synthesis of iridoid-glycosides[18] as well as in the preparation of orthoester structures on hexonolactones[19]. 55 The present work shows that trimethylsilyltriflate is particularly useful for the linking to oligosaccharides of hydroxyl groups which are known to be weakly reactive; however, for this reaction it is necessary to carefully select a type of protective group both for the glycosyl donor as well as for the glycosyl acceptor. In this way the new process represents a worthwhile extension of the methods for oligosaccharide synthesis used to date.

Discussion and Results

The easily-obtained azidonitrate[5] 1 is the starting material for the preparation of the synthesis building block β-D-Galp-(1→3)-D-$GalN_3$. During further exchange reactions, it is necessary to introduce a temporary protection at O-1 by means of glycosidation as methyl or allyl glycoside. The formation of the glycoside of 2-azido-2-desoxy-D-galactose from 1 is always carried out via the 1-acetate and then the pyranosyl bromide. We discovered that this circuituous route is not necessary; the nitrate group can also function as an excellent leaving group in a glycosidation reaction. In addition, it is possible to arrange the azidonitration in order to produce the crystalline α-nitrate virtually exclusively. Subsequent reaction with sodium methylate produces in one step a complete inversion (95%) to the β-glycoside 2. Using sodium allylate, 1 may be converted analogously to the allyl glycoside 4 with the same yield. The glycosides 2 and 4 both yield upon acetylation the triacetates 3 and 5. The versatility of this new method using the nitrate as leaving group is demonstrated by the reaction involving the azidonitrate of lactose 6, which undergoes isomerization with lithium nitrate to produce the virtually pure α-form.

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* Translator's note: this should read "trimethylsilyltrifluoromethanesulfate".

The reaction of 6 with sodium methylate involves an inversion to produce directly the methyl-β-D-glycoside 12 in high yield; this was characterized in the form of the corresponding hexaacetate 13 by ^{1}H-nmr spectroscopy. We are carrying out further experiments to determine whether the nitrate is also suitable as a leaving group for the analogous disaccharide syntheses.

From 2 and 4 a series of glycosyl acceptors, not substituted at OH-3, were synthesized for preparation of β-D-Galp-(1→3)-D-GalNAc. The reaction of 2 with 2,2-dimethyoxypropane under kinetically-controlled conditions produces 7 . The formation of the 4,6-O-isopropylidene compound 7 was verified by ^{1}H-nmr spectroscopy after acetylation to the monoacetate. In the same way 2 was reacted with dimethoxytoluene to produce the derivative 8 . Selectively benzoylated derivatives are obtained by the reaction of 2 with 2.25 moles benzoyl cyanide at 10°. Under these conditions 70% of the 4,6-di-O-benzoylated compound 11 can easily be separtaed by chromatography from the 6-benzoate 28 and the corresponding tribenzoate formed as side-products in the reaction. In an analogous way the partially-protected product 10 is prepared from the allylglycoside 4 . Both of the known halides 9 [20] and 17 [21] were used as glycoside donors.

Under Koenigs-Knorr conditions, coupling products of the halides 56
are observed only with the use of mercury catalysts in nitromethane-toluene, particularly under unfavourable reaction conditions. Thus, under these conditions the reaction of 9 with 7 gives the undesired β-(1→6)-glycosidic coupled disaccharides 14 and 15 . Apparently under those reaction conditions the 4,6-O-isopropylide group is converted to the 3,4-O-substituted product, which then undergoes a glycoside synthesis with the OH-6 group. Some of 14 hydrolyzes further to 15 . After acidic hydrolysis of the disaccharide mixture one obtains pure 15 which can be acetylated to 16 . The ^{1}H-nmr spectral analysis of 16 clearly shows that OH-3 and -4 are acetylated and OH-6 is glycosidated.

In the reaction of 9 with 8 , and 9 with 11 , preactically no reaction products are formed. The halide 9 is observed to be nearly 57
completely hydrolyzed. Only with the halide 17 which is significantly more reactive then 9 because of the presence of three benzylether

groups, is the β-(1→3)-glycoside linked product 20 obtained with 11 , although the yield is poor (10%). The type of linkage is determined using ^{1}H-nmr spectroscopy on the acetylated product 21 . The very slight reactivity of the OH-3 group in the various glycosyl acceptors 7 , 8 and 11 is apparent from these studies. These results provided a stimulus to explore the Lewis acid catalyzed glycosidation as an alternative route.

For the Lewis acid catalyzed reactions, only those reactants having acid-stable protective groups can be considered. Therefore the glycosyl acceptor 11 was selected first for reaction with the pentaacetate 19 [20]. Even using $FeCl_3$ as catalyst, the reaction of 11 with 19 produced the desired disaccharide 22 with a 30% yield. For the weaker Lewis acid $HgBr_2$, the yield was smaller. With the stronger Lewis acids BF_3 and $SnCl_4$ side reactions became increasingly important and thereby reduced the yields. The best conditions arose with trimethylsilyltriflate in the presence of MOLSIEB 4A° (molecular sieves). In dichloromethane, 11 could be reacted with 19 at 20° for 4 hours to produce the disaccharide 22 in 85% yield. This fundamental structure for the formation of synthesis building blocks was therefore readily available. The very useful hexaacetate 23 was obtained from 22 after removal of acyl groups and subsequent acetylation. An analogous reaction of the allylglycoside 10 with 19 produces the corresponding disaccharide 24 ; after deacylation and subsequent acetylation the pure acetate 25 can be isolated. All structures were established using ^{1}H-nmr spectroscopy.

The glycosyl acceptor 11 may be reacted with the β-acetate 18 [21] , which has a higher reactivity due to the three benzylether substituents, in the presence of trimethylsilyltriflate to yield the disaccharide 20 in nearly the same way as for 22. The product is converted to the acetate 21 after debenzoylation. The benzyl ether groups are still sufficiently acid-stable in this case. This is, however, not generally true. Unwanted ether cleavage, which causes side reactions, occurs relatively often. Compounds containing o-isopropylidene groups cannot be reacted according to the procedure described here. The reaction of 7 with 19 in the presence of trimethylsilyltriflate for a 5 minute reaction time at 20° yields nearly

quantitatively the β-(1→6) coupled disaccharide 14. Apparently a rapid transfer of the o-isopropylidene groups occurs.

The success of the trimethylsilyltriflate catalyzed reaction in the synthesis of 22 encouraged us to try other glycoside syntheses, in particular those reactions involving the linking of exceptionally weakly reactive hydroxyl groups to another saccharide unit. During the selective benzoylation of 2 , the monobenzoate 28 with free OH-3 and OH-4 groups is also formed. In the presence of trimethylsilyltriflate this reacts with 2 moles of the glycosyl donor 19 simultaneously to give the branched trisaccharide 29, which after debenzoylation can be isolated in 51% yield as the nonaacetate 30 . The reaction is remarkable in that the OH-3 and -4 glycosidated derivative of the D-galactose has only been prepared in the past by using the corresponding "step-by-step" synthesis[22,23]. Using the ^{1}H-nmr spectrum, the type 58
of linkage in 30 may be identified from the values H-1" δ4.98, $J_{1",2"}$ 8.0 Hz; H-1' δ4.70, $J_{1',2'}$ 7.8 Hz and H-1 δ4.09, $J_{1,2}$ 8.0 Hz

The 1,6-anhydro compound 26 reacts with 19 in the presence 59
of trimethylsilyltriflate to form the disaccharide 27. This unit is the essential part of the core-B-structure of O-glycoproteins[24]. A corresponding synthesis building block for the β-D-Galp-(1→3)-D-Gal unit can be developed from 27. However, subsequently we discovered another route to the formation of this building block, which avoids the use of the relatively expensive 1,6-anhydro-D-galactose[25]. Previous procedures used to synthesize this unit under Koenigs-Knorr conditions are considered to be unsatisfactory[26,27].

Peracetylated β-acetates of disaccharides are also suitable as glycosyl donors. Thus, the lactose derivative 33 reacts with the glycosyl acceptor 11 to give the trisaccharide 35 in 55% yield. When one considers the lower reactivity of 33 compared to 19 , this is a very satisfactory result.

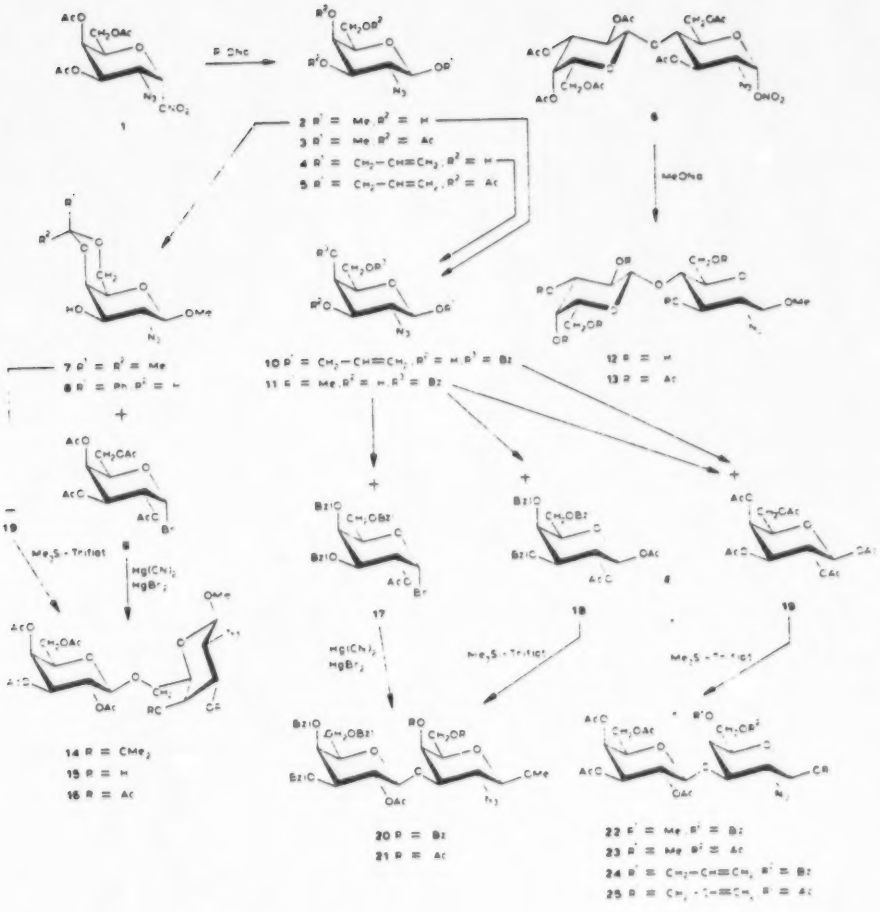
For the preparation of the lactosamine derivative 32, a series of very good processes are known whereby 31 is reacted with 2,3,4,6-tri-O-acetyl-β-D-galactopyranosyl bromide[28-31]. In principle, however, the relatively unreactive OH-4 group of 31 may also be reacted directly with β-acetates by the method described here. Thus the reaction of 19 with 31 in the presence of trimethylsilyltriflate produces 32; the reaction of the phthalimido derivative 36 with 31 under analogous

conditions produces the chitobiose derivative 34. It should, however, be pointed out that with other benzylether-containing glycosyl acceptors cleavage of benzylether can occur under the relatively acidic conditions.

All of the examples demonstrate that the new procedure is both simplified and efficient. However, it must be emphasized that the glycosidation by the trimethylsilyltriflate process only operates stereoselectively if the glycosyl donor is a β-acetate (1,2-trans-acetate) and if the C-2 contains an adjacent active substituent, such as an acetyl group. α-acetates (1,2-cis-acetates) do not undergo corresponding reactions since in this case the neighbouring group can not contribute to the weakening of the acetate linkage. This fact indicates that the neighbouring group does participate in these reactions, and this controls the stereoselectivity of the reaction.

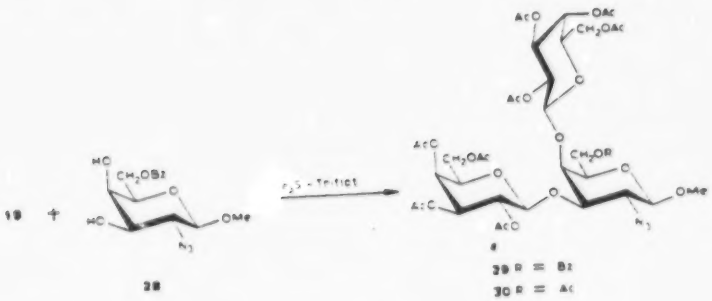
The exact mechanism of the Lewis acid catalyzed glycosidation has not yet been elucidated in complete detail. All findings thus far are in agreement on the first step: with neighbouring group participation the Lewis acid catalyst converts the peracetylated sugar into a cyclic 1,2-O-dioxocarbenium ion. Depending on the type of Lewis acid, the ion is stabilized either as a complex or as an ion pair[32,33]. The selective trans opening penetration of the 1,2-O-dioxocarbenium ion by a nucleophile could occur directly or via an activated intermediate of the aglycone. In the case of the trimethylsilyltriflate catalyzed reaction, the trifluoromethanesulfonic acid thereby liberated presumably exists in equilibrium with the acetic acid trimethylsilyl ester formed in the first reaction step. The equilibrium should lie on the trifluoromethanesulfonic acid side in order to maintain a constant catalytic effect. The excess of the trifluoromethanesulfonic acid is apparently trapped due to an equilibrium involving the MOLSIEB 4A (molecular sieves). 60

It was found that the trimethylsilyltriflate catalyzed reaction only proceeds in good yield under weakly acidic conditions. In the presence of a base , the OH-free components undergo silylation to form silyl ethers which then react further in undesirable ways. Thus for substance 28 which is unsubstituted at OH-3 and OH-4, reaction with trimethylsilyltriflate in the presence of pyridine produces nearly quantitatively the 3,4-di-O-trimethylsilylated product of 28 .



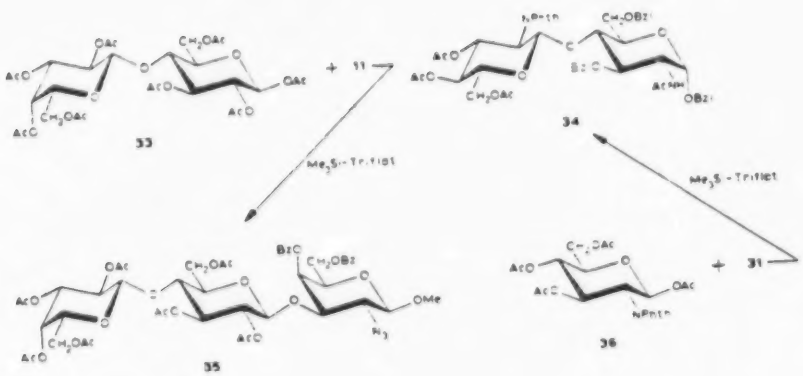
56

26 27



28 29 R = Bz 30 R = Ac

31 32



33 34 35 36

Experimental Section

General Methods

All reactions were monitored using thin-layer chromatography on silica gel coated aluminum foil (MERCK GF_{254}). Mobile phases: ethyl acetate-petroleum ether, ether-petroleum ether, toluene-acetone, chloroform-methanol, chloroform-methanol-water, ethyl acetate-methanol-water. Detector: UV absorption, spraying with 10% ethanolic sulfuric acid and heating. Preparative column chromatography: silica gel 60 (70-230 mesh, MERCK). Melting points: LEITZ heating stage microscope, not calibrated. Optical rotations: PERKIN-ELMER polarimeter 241 or 243 in 1-dm cells at 589 nm (Na-D line). ^{1}H-nmr spectra: BRUKER NH 270 or WM 400, inner standard Me_4Si.

All of the reagents and solvents used for the glycoside syntheses were absolutely anhydrous, and were stored over MOLSIEB (4A). The glycoside syntheses were always carried out under the most stringent anhydrous conditions to eliminate any traces of moisture.

Methyl-2-azido-2-desoxy-β-D-galactopyranoside (2)

Compound 1 (reference [18]; 10 g, 26.5 mmol) was suspended in methanol (50 mL), sodium (0.69 g, 30.0 mmol) added. After 30 minutes this was neutralized with AMBERLITE IRC 50 ion exchanger. The solution was filtered and then concentrated down *in vacuo*. The sodium nitrate formed in the reaction was separated off by taking up the syrupy reaction product in methanol-acetone (1:3, v/v), followed by filtration and concentration *in vacuo* of the solution; yield: 5.5 g (95%), syrup, $[\alpha]_D^{24}$ -72° (c 1, methanol).

Analysis: for $C_7H_{13}N_3O_5$ (219.2) Reported: C 38.36 H 5.98 N 19.17
Found: C 38.59 H 6.02 N 20.01

Methyl-3,4,6-tri-O-acetyl-2-azido-2-desoxy-β-D-galactopyranoside (3)

Compound 2 (22 mg, 0.1 mmol) was dissolved in pyridine (2 mL) and acetic anhydride (0.5 mL). After 6 hours, the solution was concentrated down in vacuo; yield: 30 mg (87%), syrup, $[\alpha]_D^{24}$ -18° (c 0.3, methanol).

^{1}H-N.m.r. (270 MHz, $CDCl_3$): δ 5.33 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 1.0 Hz, H-4), 4.81 (dd, 1 H, $J_{2,3}$ 11.0, $J_{3,4}$ 3.4 Hz, H-3), 4.30 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.19 (dd, 1 H, $J_{5,6a}$ 6.6, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.14 (dd, 1 H, $J_{5,6b}$ 4.1, $J_{6a,6b}$ 11.4 Hz, H-6b), 3.87 (ddd, 1 H, $J_{4,5}$ 1.0, $J_{5,6a}$ 6.6, $J_{5,6b}$ 4.1 Hz, H-5), 3.67 (dd, 1 H, $J_{1,2}$ 8.0, $J_{2,3}$ 11.0 Hz, H-2), 3.61 (s, 3 H, OMe), 2.17, 2.08 (2 s, 9 H, 3 OAc).

Analysis: for $C_{13}H_{19}N_3O_8$ (345.3) Reported: C 45.22 H 5.55 N 12.17 61
Found: C 45.40 H 5.78 N 12.31

Allyl-2-azido-2-desoxy-β-D-galactopyranoside (4)

Compound 1 (10 g, 26.5 mmol) was suspended in allyl alcohol (50 mL) and sodium (0.698 g, 30 mmol) was added. After 30 minutes, the treatment described for 2 was carried out; yield: 6.3 g (97%), syrup, $[\alpha]_D^{20}$ -61° (c 0.1, methanol).

Analysis: for $C_9H_{15}N_3O_5$ (245.2) Reported: C 44.08 H 6.17 N 17.13
Found: C 44.54 H 6.23 N 17.00

Allyl-3,4,6-tri-O-acetyl-2-azido-2-desoxy-β-D-galactopyranoside (5)

Compound 4 (25 mg, 0.1 mmol) was acetylated as described for 3 ; yield: 35 mg (94%), syrup, $[\alpha]_D^{24}$ -20° (c 0.2, methanol)

^{1}H-N.m.r. (270 MHz, $CDCl_3$): δ 5.31 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 0.8 Hz, H-4), 4.76 (dd, 1 H, $J_{2,3}$ 11.0, $J_{3,4}$ 3.4 Hz, H-3), 4.40 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.16 (dd, 1 H, $J_{5,6a}$ 6.0, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.11 (dd, 1 H, $J_{5,6b}$ 7.0, $J_{6a,6b}$ 12.0 Hz, H-6b), 3.85 (ddd, 1 H, $J_{4,5}$ 0.8, $J_{5,6a}$ 6.0, $J_{5,6b}$ 7.0 Hz, H-5), 3.70 (dd, 1 H, $J_{1,2}$ 8.0, $J_{2,3}$ 11.0 Hz, H-2), 2.13, 2.05 (2 s, 9 H, 3 OAc).

Analysis: for $C_{15}H_{20}N_3O_8$ (370.4) Reported: C 48.65 H 5.44 N 11.35
Found: C 49.16 H 5.54 N 11.46

Methyl-2-azido-2-desoxy-4,6-O-isopropylidene-β-D-galactopyranoside (7)

Compound 2 (1.1 g, 5 mmol) was dissolved in N,N-dimethylformamide (10 mL) and 2,2-dimethyloxypropane (6 mL) along with p-toluenesulfonic acid (50 mg) were added. After 6 hours the solution was neutralized with triethylamine (1 mL) and then concentrated down in vacuo. The syrupy reaction mixture was chromatographed on silica gel (ethyl acetate-petroleum ether 2:1, v/v); yield: 1.04 g (78%), syrup, $[\alpha]_D^{24}$ -8° (c 1.0, methanol).

^{1}H-N.m.r. (270 MHz, $CDCl_3$): δ 4.31 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 0.8 Hz, H-4), 4.21 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.00 (dd, 1 H, $J_{5,6a}$ 2.4, $J_{6a,6b}$ 12.6 Hz, H-6a), 3.90 (dd, 1 H, $J_{5,6b}$ 1.3, $J_{6a,6b}$ 12.6 Hz, H-6b), 3.80 (dd, 1 H, $J_{1,2}$ 8.0, $J_{2,3}$ 10.4 Hz, H-2), 3.28 (m, 1 H, H-5), 3.10 (dd, 1 H, $J_{2,3}$ 10.4, $J_{3,4}$ 3.4 Hz, H-3), 1.51, 1.42 (2 s, 6 H, 2 Me_2C).

Analysis: for $C_{10}H_{17}N_3O_5$ (259.3) Reported: 46.33 H 6.61 N 16.21
Found: 46.41 H 6.98 N 16.45

A sample (25 mg, 0.1 mmol) was acetylated overnight at 20° in pyridine (2 mL) and acetic anhydride (0.5 mL). Then the solution was concentrated down in vacuo; yield: 28 mg (93%), syrup, $[\alpha]_D^{24}$ -12° (c 0.3, methanol).

Ausb. 28 mg (93%), Sirup. $[\alpha]_D^{24}$ −12° (c 0.3, Methanol); ^{1}H-N.m.r. (270 MHz, $CDCl_3$): δ 4.66 (dd, 1 H, $J_{2,3}$ 10.8, $J_{3,4}$ 3.4 Hz, H-3), 4.28 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 0.9 Hz, H-4), 4.19 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.06 (dd, 1 H, $J_{5,6a}$ 2.1, $J_{6a,6b}$ 12.8 Hz, H-6a), 3.96 (dd, 1 H, $J_{5,6b}$ 1.6, $J_{6a,6b}$ 12.8 Hz, H-6b), 3.82 (dd, 1 H, $J_{1,2}$ 7.8, $J_{2,3}$ 10.8 Hz, H-2), 3.59 (s, 3 H, OMe), 3.34 (ddd, 1 H, $J_{4,5}$ 0.9, $J_{5,6a}$ 2.1, $J_{5,6b}$ 1.6 Hz, H-5), 2.15 (s, 3 H, 1 OAc), 1.45, 1.41 (2 s, 6 H, 2 Me_2C).

Analysis: for $C_{12}H_{19}N_3O_6$ (301.3) Reported: C 47.84 H 6.36 N 13.95
Found: C 48.10 H 6.51 N 14.02

Methyl-2-azido-4,6-O-benzylidene-2-desoxy-β-D-galactopyranoside (8)

Compound 2 (1.1 g, 5 mmol) was dissolved in absolute nitromethane (10 mL) and treated with α,α-dimethoxytoluene (8 mL) as well as p-toluenesulfonic acid (50 mg) at 20°. The reaction finishes in about 2 hours, and then the treatment described for compound (7) was carried out; yield: 1.1 g (68%), syrup $[\alpha]_D^{26}$ -14° (c 0.1, methanol ^{1}H-N.m.r. (270 MHz 62 $CDCl_3$): δ 7.40–7.18 (m, 5 H, Ph), 5.40 (s, 1 H, PhCH), 4.40 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.22 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 0.6 Hz, H-4), 3.82 (m, 1 H, H-5), 3.71 (dd, 1 H, $J_{2,3}$ 10.8, $J_{3,4}$ 3.4 Hz, H-3), 3.61 (dd, 1 H, $J_{1,2}$ 8.0, $J_{2,3}$ 10.8 Hz, H-2).

Analysis: for $C_{16}H_{17}N_3O_5$ (331.3) Reported: C 58.00 H 5.77 N 12.68
Found: C 58.06 H 5.24 N 13.10

Allyl-2-azido-4,6-di-O-benzoyl-2-desoxy-β-D-galactopyranoside (10)

Compound 4 (4.9 g, 20 mmol) was dissolved in absolute pyridine (20 mL) and benzoylated at 5-8° with benzoyl cyanide (5.9 g, 45 mmol) in dichloromethane (20 mL) as described for compound 11; yield: 5.6 g (62.5%), syrup, $[\alpha]_D^{24}$ -32° (c 0.1, methanol); ^{1}H-N.m.r. (270 MHz, $CDCl_3$): δ 8.14–7.47 (m, 10 H, Ph), 5.96 (dddd, 1 H, H-1, OAll), 5.64 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 0.8 Hz, H-4), 4.57 (dd, 1 H, $J_{5,6a}$ 7.0, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.43 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.34 (dd, 1 H, $J_{5,6b}$ 6.3, $J_{6a,6b}$ 11.4 Hz, H-6b), 4.01 (ddd, 1 H, $J_{4,5}$ 0.8, $J_{5,6a}$ 7.0, $J_{5,6b}$ 6.3 Hz, H-5), 3.73 (dd, 1 H, $J_{2,3}$ 10.4, $J_{3,4}$ 3.4 Hz, H-3), 3.67 (dd, 1 H, $J_{1,2}$ 7.8, $J_{2,3}$ 10.5 Hz, H-2).

Analysis: for $C_{23}H_{23}N_3O_7$ (453.5) Reported: C 60.92 H 5.11 N 9.27
Found: C 60.52 H 5.30 N 9.36

Methyl-2-azido-4,6-di-O-benzoyl-2-desoxy-β-D-galactopyranoside (11)

Compound 2 (4.4 g, 20 mmol) was dissolved in absolute pyridine (20 mL) and treated at 8-10° dropwise with benzoyl cyanide (5.9 g, 45 mmol) in dichloromethane (20 mL) over a period of 2 hours. The reaction progress was monitored by thin-layer chromatography (ethyl acetate-petroleum ether 2:3, v/v). After 24 hours the reaction was complete. Methanol (20 mL) was added and then after 30 minutes the mixture was concentrated down in vacuo. The syrupy reaction product was chromatographed on silica gel (ethyl acetate-petroleum ether 2:3, v/v); yield: 6.2 g (70%), melting point 32°, $[\alpha]_D^{24}$ -18° (c 0.7, methanol).

^{1}H-N.m.r. (270 MHz, $CDCl_3$): δ 8.31–7.40 (m, 10 H, Ph), 5.67 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 1.0 Hz, H-4), 4.60 (dd, 1 H, $J_{5,6a}$ 6.4, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.37 (dd, 1 H, $J_{5,6b}$ 6.2, $J_{6a,6b}$ 11.4 Hz, H-6b), 4.33 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.06 (ddd, 1 H, $J_{4,5}$ 1.0, $J_{5,6a}$ 6.4, $J_{5,6b}$ 6.2 Hz, H-5), (dd, 1 H, $J_{2,3}$ 10.4, $J_{3,4}$ 3.4 Hz, H-3), 3.67 (dd, 1 H, $J_{1,2}$ 8.0, $J_{2,3}$ 10.4 Hz, H-2).

Analysis: for $C_{21}H_{21}N_3O_7$ (427.4) Reported: C 59.01 H 4.95 N 9.83
Found: C 60.04 H 5.12 N 10.04

Methyl-3,6-di-O-acetyl-2-azido-2-desoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-β-D-glycopyranoside (13)

Compound 6 (reference [18]; 133 mg, 0.2 mmol) was suspended in methanol (5 mL) and treated with sodium (60 mg). After 1 hour the treatment described for compound 2 was carried out; the compound 12 obtained was acetylated in pyridine (3 ml) and acetic anhydride (1 mL), then the treatment described for compound 4 was carried out; yield: 120 mg (95%), syrup, $[\alpha]_D^{24}$ +8° (c 0.5, methanol). ^{1}H-N.m.r. (270 MHz, $CDCl_3$): δ 5.46 (dd, 1 H, $J_{2,3}$ 10.6, $J_{3,4}$ 9.0 Hz, H-3), 5.36 (dd, 1 H, $J_{3',4'}$ 3.4, $J_{4',5'}$ 1.2 Hz, H-4'), 5.12 (dd, 1 H, $J_{1',2'}$ 8.0 $J_{2',3'}$ 10.4 Hz, H-2'), 4.95 (dd, 1 H, $J_{2',3'}$ 10.4, $J_{3',4'}$ 3.4 Hz, H-3'), 4.55 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.49 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 3.89 (m, 2 H, H-5',5), 3.71 (dd, 1 H, $J_{3,4}$ 9.0, $J_{4,5}$ 9.2 Hz, H-4), 3.44 (s, 3 H, OMe), 3.19 (dd, 1 H, $J_{1,2}$ 7.8, $J_{2,3}$ 10.6 Hz, H-2), 2.15, 2.12, 2.04 (6 s, 18 H, 6 OAc).

Analysis: for $C_{25}H_{35}N_3O_{16}$ (633.6) Reported: C 47.39 H 5.57 N 6.63 63
Found: C 47.46 H 5.62 N 6.70

Methyl-2-azido-2-desoxy-3,4-O-isopropylidene-6-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-β-D-galactopyranoside (14) and methyl-2-azido-2-desoxy-6-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-β-D-galactopyranoside (15)

A solution of 7 (260 mg, 1 mmol) in absolute toluene-nitromethane (10 mL, 1:1, v/v) was treated with mercury (II) cyanide (260 mg) and mercury (II) bromide (36 mg) along with molecular sieves 4A (500 mg), and then the mixture was stirred for 1 hour at 60°. Then while stirring was continued at 60°, a solution of 9 (1.1 g, 2.5 mmol) in absolute toluene-nitromethane (15 mL, 1:1, v/v) was added dropwise over a period of 3 hours. Stirring was continued at 60° for another 4 hours. After cooling, the solution was diluted with chloroform (20 mL) and then filtered through CELITE, washed to neutrality with $NaHCO_3$ solution and water, dried with $MgSO_4$ and concentrated down in vacuo. The mixture of products was chromatographed on silica gel (ethyl acetate-petroleum ether 1:1, v/v) to produce compounds 14 and 15 .

Compound 14 — Yield: 206 mg (35% relative to 7), syrup, $[\alpha]_D^{24}$ +10° (c 0.1, acetone).

^{1}H-N.m.r. (400 MHz, $CDCl_3$): δ 5.41 (dd, 1 H, $J_{3',4'}$ 3.4, $J_{4',5'}$ 1.0 Hz, H-4'), 5.22 (dd, 1 H, $J_{1',2'}$ 7.8, $J_{2',3'}$ 10.5 Hz, H-2'), 5.01 (dd, 1 H, $J_{2',3'}$ 10.5, $J_{3',4'}$ 3.4 Hz, H-3'), 4.61 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1'), 4.10 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.03 (dd, 1 H, $J_{3,4}$ 5.2, $J_{4,5}$ 2.0 Hz, H-4), 3.94 (dd, 1 H, $J_{1,2}$ 8.0, $J_{2,3}$ 8.4 Hz, H-2), 3.58 (s, 1 H, OMe), 2.17, 2.15, 2.05, 2.02 (4 s, 12 H, 4 OAc), 1.52, 1.33 (2 s, 6 H, 2 Me_2C).

Analysis: for $C_{24}H_{35}N_3O_{14}$ (589.6) Reported: C 48.90 H 5.98 N 7.13
Found: C 48.81 H 5.69 N 7.25

Compound 15 — Yield: 110 mg (20% relative to 7), syrup, $[\alpha]_D^{24}$ -40° (c 0.1, acetone).

^{1}H-N.m.r. (400 MHz, $CDCl_3$): δ 5.40 (dd, 1 H, $J_{3',4'}$ 3.4, $J_{4',5'}$ 0.8 Hz, H-4'), 5.20 (dd, 1 H, $J_{1',2'}$ 7.8, $J_{2',3'}$ 10.5 Hz, H-2'), 5.05 (dd, 1 H, $J_{2',3'}$ 10.5, $J_{3',4'}$ 3.4 Hz, H-3'), 4.60 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1'), 4.17 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.00 (dd, 1 H, $J_{5',6'a}$ 6.6, $J_{6'a,6'b}$ 10.6 Hz, H-6'a), 3.93 (dd, 1 H, $J_{5',6'b}$ 6.4, $J_{6'a,6'b}$ 10.6 Hz, H-6'b), 3.57 (s, 3 H, OMe), 3.05, 2.93 (2 s, 2 H, OH), 2.15, 2.14, 2.06, 2.05 (4 s, 12 H, 4 OAc).

Analysis: for $C_{21}H_{31}N_3O_{14}$ (549.5) Reported: C 45.90 H 5.69 N 7.65
Found: C 45.95 H 5.81 N 7.49

Methyl-3,4-di-O-acetyl-2-azido-2-desoxy-6-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-β-D-galactopyranoside (16)

Compound 15 (11 mg, 0.02 mmol) was acetylated at 20° in pyridine (2 mL) and acetic anhydride (0.5 mL). After 6 hours the solution was concentrated down in vacuo; yield: 12 mg (95%), syrup, $[\alpha]_D^{24}$ -28° (c 0.1, chloroform).

^{1}H-N.m.r. (400 MHz, $CHCl_3$): δ 5.39 (dd, 1 H, $J_{3',2'}$ 3.4, $J_{4',5'}$ 0.5 Hz, H-4'), 5.32 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 0.8 Hz, H-4), 5.17 (dd, 1 H, $J_{1',2'}$ 7.8, $J_{2',3'}$ 10.4 Hz, H-2'), 4.99 (dd, 1 H, $J_{2',3'}$ 10.4, $J_{3',4'}$ 3.4 Hz, H-3'), 4.78 (dd, 1 H, $J_{2,3}$ 11.0, $J_{3,4}$ 3.4 Hz, H-3), 4.52 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1'), 4.27 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.18 (dd, 1 H, $J_{5',6'a}$ 6.6, $J_{6'a,6'b}$ 11.4 Hz, H-6'a), 4.11 (dd, 1 H, $J_{5',6'b}$ 7.4, $J_{6'a,6'b}$ 11.4 Hz, H-6'b), 3.90 (m, 1 H, H-5'), 3.64 (dd, 1 H, $J_{1,2}$ 8.0, $J_{2,3}$ 11.0 Hz, H-2), 3.60 (s, 3 H, OMe), 2.15, 2.12, 2.06, 2.04, (4 s, 18 H, 6 OAc). 64

Analysis: for $C_{25}H_{35}N_3O_{16}$ (633.6) Reported: C 47.39 H 5.57 N 6.63
Found: C 47.68 H 5.39 N 6.70

2-O-acetyl-3,4,6-tri-O-benzyl-α-D-galacto-pyranosylbromide (17)

Compound 18 (reference [20]; 0.5 g, 0.98 mmol) was dissolved in dichloromethane (8 mL) and ethyl acetate (0.2 mL) then treated with $TiBr_4$ (0.4 g). After 30 minutes the mixture was neutralized with sodium acetate, filtered over CELITE and concentrated down in vacuo; yield: 0.43 g (79%), syrup, $[\alpha]_D^{24}$ +41° (c 0.3, chloroform).

^{1}H-N.m.r. (400 MHz, $CDCl_3$): δ 7.32–7.28 (m, 15 H, Ph), 5.84 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1), 5.42 (dd, 1 H, $J_{1,2}$ 3.2, $J_{2,3}$ 10.4 Hz, H-2), 4.00 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 0.6 Hz, H-4), 3.64 (dd, 1 H, $J_{2,3}$ 10.4, $J_{3,4}$ 3.4 Hz, H-3), 2.05 (s, 3 H, OAc).

Analysis: for $C_{24}H_{32}BrN_3O_{15}$ (682.4)

Reported:	C 42.24	H 4.73	Br 11.70	N 6.16
Found:	C 42.26	H 4.90	Br 12.00	N 6.19

Methyl-4,6-di-O-acetyl-3-O-(2-O-acetyl-3,4,6-tri-O-benzyl-β-D-galactopyranosyl)-2-azido-2-desoxy-β-D-galactopyranoside (21)

A solution of 11 (440 mg, 1 mmol) in absolute toluene-nitromethane (10 mL, 1:1, v/v) was treated with $Hg(CN)_2$ (260 mg) and $HgBr_2$ (36 mg) along with molecular sieves 4A (500 mg) and then stirred at 20° for 1 hour. Then, while stirring at 20°, a solution of 17 (540 mg, 1.0 mmol) in absolute toluene (10 mL) was added dropwise over a period of one hour. Stirring was continued for another 6 hours at 20°, and then the treatment described for 14 was carried out. The reaction product was dissolved in methanol (10 mL) and 1% sodium methoxide solution was added dropwise to a pH value of 11. After 8 hours at 20° the reaction is complete; the solution was neutralized with AMBERLITE IRC-50 ion exchanger, filtered and concentrated down in vacuo, then taken up in pyridine (5 mL) and acetic anhydride (2 mL). After 4 hours the solution was concentrated down in vacuo. The reaction product was chromatographed on silica gel (ethyl acetate-petroleum ether 1:2, v/v); yield: 56 mg (7.5%), syrup, $[\alpha]_D^{24}$ -12° (c 0.6, chloroform).

^{1}H-N.m.r. (400 MHz, $CDCl_3$): δ 7.36–7.27 (m, 15 H, Ph), 5.32 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 0.5 Hz, H-4), 5.30 (dd, 1 H, $J_{1',2'}$ 7.8, $J_{2',3'}$ 10.4 Hz, H-2'), 4.54 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1'), 4.13 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 3.93 (dd, 1 H, $J_{3',4'}$ 3.0, $J_{4',5'}$ 0.8 Hz, H-4'), 3.66 (m, 1 H, H-5'), 3.57 (dd, 1 H, $J_{1,2}$ 8.0, $J_{2,3}$ 10.2 Hz, H-2), 3.53 (s, 3 H, OMe), 3.51 (dd, 1 H, $J_{2',3'}$ 10.4, $J_{3',4'}$ 3.0 Hz, H-3'), 3.46 (dd, 1 H, $J_{2,3}$ 10.2, $J_{3,4}$ 3.4 Hz, H-3), 2.10, 2.04, 2.02 (3 s, 9 H, 3 OAc).

Analysis: for $C_{37}H_{48}N_3O_{13}$ (742.8) Reported: C 59.83 H 6.51 N 5.66

Found: C 60.01 H 6.29 N 5.68

Formation of 21 from 18 and 11 using trimethylsilyl-trifluoromethanesulfonate (trimethylsilyltriflate) catalysis

Compound 11 (110 mg, 0.25 mmol) and 18 (reference [20]; 125 mg, 0.25 mmol) were dissolved in absolute dichloromethane (10 mL), and stirred for 1 hour at 20° with molecular sieves (500 mg, spherical). Trimethylsilyltriflate (20 µL) was added. After 2-24 hours at 20° the reaction was complete. The mixture was neutralized with absolute triethylamine, then filtered and concentrated down in vacuo. The reaction product was dissolved in methanol (10 mL) and treated with 1% sodium methoxide solution at pH 11. After 8 hours at 20° the reaction was complete. 65
The mixture was neutralized with AMBERLITE IRC-50, filtered, concentrated down in vacuo and then taken up in pyridine (5 mL) and acetic acid (2 mL). After 4 hours the product was concentrated down in vacuo. Then it was purified on silica gel (ethyl acetate-petroleum ether 1:1, v/v); yield: 128 mg (69%). The analytical data for this product are identical to the values for the same compound prepared using the Koenigs-Knorr process.

Methyl-2-azido-4,6-di-O-benzoyl-2-desoxy-3-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-β-D-galactopyranoside (22)

Compound 11 (4.3 g, 10 mmol) and 19 (3.5 g, 9 mmol) were dissolved in absolute 1,2-dichloroethane (50 mL) and stirred with molecular sieves 4A (10 g) for 1 hour at 20°. Then trimethylsilyl-triflate (0.2 mL) was added and stirred again for 6 hours at 20°. The mixture was neutralized with triethylamine, filtered, and concentrated down in vacuo. The syrupy reaction product was purified by column chromatography (ethyl acetate-petroleum ether 1:1.7, v/v); yield: 5.5 g (71%), syrup, $[\alpha]_D^{20}$ -52° (c 0.1, chloroform).
^{1}H-N.m.r. (400 MHz, $CDCl_3$): δ 8.10–7.35 (m, 10 H, Ph), 5.44 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 0.8 Hz, H-4), 5.35 (dd, 1 H, $J_{1',2'}$ 8.0, $J_{2',3'}$ 10.4 Hz, H-2'), 5.32 (dd, 1 H, $J_{3',4'}$ 3.2, $J_{4',5'}$ 0.8 Hz, H-4'), 4.97 (dd, 1 H, $J_{2',3'}$ 10.4, $J_{3',4'}$ 3.2 Hz, H-3'), 4.85 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 4.49 (dd, 1 H, $J_{5,6a}$ 5.0, $J_{6a,6b}$ 11.6 Hz, H-6a), 4.42 (dd, 1 H, $J_{5,6b}$ 7.2, $J_{6a,6b}$ 11.6 Hz, H-6b), 4.27 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.17 (dd, 1 H, $J_{5',6'a}$ 6.8, $J_{6'a,6'b}$ 11.4 Hz, H-6'a), 4.12 (dd, 1 H, $J_{5',6'b}$ 6.2, $J_{6'a,6'b}$ 11.4 Hz, H-6'b), 4.06 (ddd, 1 H, $J_{4',5'}$ 0.8, $J_{5',6'a}$ 6.8, $J_{5',6'b}$ 6.2 Hz, H-5'), 3.89 (ddd, 1 H, $J_{4,5}$ 0.8 $J_{5,6a}$ 5.0, $J_{5,6b}$ 7.2 Hz, H-5), 3.78 (dd, 1 H, $J_{1,2}$ 7.8, $J_{2,3}$ 10.6 Hz, H-2), 3.68 (dd, 1 H, $J_{2,3}$ 10.6, $J_{3,4}$ 3.4 Hz, H-3), 3.63 (s, 3 H, OMe), 2.18, 2.06, 2.01, 1.99 (4 s, 12 H, 4 OAc).

Analysis: for $C_{35}H_{39}N_3O_{16}$ (757.7) Reported: C 55.48 H 5.19 N 5.55
Found: C 55.95 H 5.16 N 5.42

Methyl-4,6-di-O-acetyl-2-azido-2-desoxy-3-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-β-D-galactopyranoside (23)

Compound 22 (780 mg, 1 mmol) was treated with methanol (5 mL). After 6 hours at 20° the reaction was complete. The mixture was neutralized with AMBERLITE IRC-50 ion exchanger, filtered, and then concentrated down in vacuo. The product was immediately dissolved in absolute pyridine (5 mL) and acetic anhydride (2 mL), and allowed to stand for 4 hours at 20°. Then it was concentrated down in vacuo and crystallized from ether-petroleum ether; yield: 620 mg (98%), melting point 184°, $[\alpha]_D^{26}$ +15° (c 0.3, chloroform).

^{1}H-N.m.r. (400 MHz, $CDCl_3$): δ 5.38 (dd, 1 H, $J_{3',4'}$ 3.4, $J_{4',5'}$ 0.8 Hz, H-4'), 5.35 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 0.8 Hz, H-4), 5.16 (dd, 1 H, $J_{1',2'}$ 7.8, $J_{2',3'}$ 10.4 Hz, H-2'), 5.01 (dd, 1 H, $J_{2',3'}$ 10.4, $J_{3',4'}$ 3.4 Hz, H-3'), 4.72 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1'), 4.18 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), 4.17 (dd, 1 H, $J_{5,6a}$ 6.2, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.10 (dd, 1 H, $J_{5',6'b}$ 1.4, $J_{6'a,6'b}$ 11.0 Hz, H-6'b), 4.08 (dd, 1 H, $J_{5,6b}$ 6.4, $J_{6a,6b}$ 11.4 Hz, H-6b), 3.90 (ddd, 1 H, $J_{4',5'}$ 0.8, $J_{5',6'a}$ 3.2, $J_{5',6'b}$ 1.4 Hz, H-5'), 3.75 (ddd, 1 H, $J_{4,5}$ 0.8, $J_{5,6a}$ 6.2, $J_{5,6b}$ 6.4 Hz, H-5), 3.60 (s, 3 H, OMe), 2.13, 2.09, 2.07, 2.06, 2.00 (5 s, 18 H, 6 OAc).

Analysis: for $C_{25}H_{35}N_3O_{16}$ (633.6) Reported: C 47.39 H 5.57 N 6.63
Found: C 47.41 H 5.60 N 6.68

Allyl-4,6-di-O-acetyl-2-azido-2-desoxy-3-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl-β-D-galactopyranoside (25) 66

Compounds 10 (450 mg, 1 mmol) and 19 (390 mg, 1 mmol) were dissolved in absolute 1,2-dichloroethane (10 mL) and then the treatment described for 22 was carried out; the reaction was complete in 6 hours. The reaction product 24 was dissolved in 1% sodium allylate solution (5 mL). After 2 hours the solution was neutralized with AMBERLITE IRC-50 ion exchanger, filtered and concentrated down in vacuo. Acetylation was carried out at 20° in pyridine (5 mL) and acetic anhydride (3 mL). After 4 hours the product was again concentrated down in vacuo. Purification was carried out by column chromatography on silica gel (ethyl acetate-petroleun ether 1:1, v/v); yield: 362 mg (55%), syrup, $[\alpha]_D^{24}$ -19° (c 0.3, chloroform). ^{1}H-N.m.r. (400 MHz, $CDCl_3$): δ 5.94 (dddd, 1 H, OAll), 5.38 (dd, 1 H, $J_{3',4'}$ 3.4, $J_{4',5'}$ 0.9 Hz, H-4'), 5.33 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 0.8 Hz, H-4), 5.17 (dd, $J_{1',2'}$ 7.8, $J_{2',3'}$ 10.4 Hz, H-2'), 5.03 (dd, 1 H, $J_{2',3'}$ 10.4, $J_{3',4'}$ 3.4 Hz, H-3'), 4.70 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1'), 4.33 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 3.87 (m, 1 H, H-5'), 3.73 (m, 1 H, H-5), 3.63 (dd, $J_{1,2}$ 8.0, $J_{2,3}$ 10.4 Hz, H-2), 3.52 (dd, $J_{2,3}$ 10.4, $J_{3,4}$ 3.4 Hz, H-3), 2.18, 2.13, 2.09, 2.08, 2.07, 2.00 (6 s, 18 H, 6 OAc).

Analysis: for $C_{27}H_{37}N_3O_{16}$ (659.6) Reported: C 49.17 H 5.65 N 6.37
Found: C 49.40 H 5.59 N 6.28

1,6-anhydro-2,4-di-O-benzyl-3-O-(2,3,4,6-tetra-O-O-acetyl-β-D-galacto-pyranosyl)-β-D-galactopyranose (27)

Compounds [34] 26 (68 mg, 0.2 mmol) and 19 (74 mg, 0.19 mmol) were reacted in dichloromethane (4 mL) as described for 22. Purification was carried out by column chromatography (ethyl acetate-petroleum ether 1:1.5, v/v); yield: 81 mg (63%), syrup, $[\alpha]_D^{24}$ -30°(c 0.3, chloroform). N.m.r. (400 MHz, $CDCl_3$): δ 7.42–7.29 (m, 10 H, Ph), 5.35 (dd, 1 H, $J_{3',4'}$ 3.4, $J_{4',5'}$ 0.8 Hz, H-4'), 5.33 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 5.19 (dd, 1 H, $J_{1',2'}$ 8.0, $J_{2',3'}$ 10.4 Hz, H-2'), 4.87 (dd, 1 H, $J_{2',3'}$ 10.4, $J_{3',4'}$ 3.4 Hz, H-3'), 4.47 (m, 1 H, H-5), 4.09 (dd, 1 H, $J_{5,6a}$ 5.6, $J_{6a,6b}$ 7.2 Hz, H-6a), 4.03 (dd, 1 H, $J_{5,6b}$ 3.0, $J_{6a,6b}$ 7.2 Hz, H-6b), 3.98 (m, 1 H, H-3), 3.88 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 3.80 (m, 1 H, H-4), 3.49 (m, 1 H, H-5'), 3.30 (s, 1 H, H-2), 2.11, 2.01, 1.97, 1.95 (4 s, 12 H, 4 OAc).

Analysis: for $C_{34}H_{40}O_{24}$ (672.7) Reported: C 60.71 H 5.99
Found: C 61.01 H 6.05

Methyl-2-azido-6-O-benzoyl-2-desoxy-β-D-galactopyranoside (28)

Compound 28 was isolated as a by-product in the column chromatography of 11; yield: 0.6 g (9.2%); melting point 158°, $[\alpha]_D^{24}$ -22° (c 0.5, methanol) ^{1}H-N.m.r. (270 MHz, $CDCl_3$): δ 8.06–7.41 (m, 5 H, Ph), 4.71 (dd, 1 H, $J_{5,6a}$ 6.8, $J_{6a,6b}$ 11.4 Hz, H-6a), 4.52 (dd, 1 H, $J_{5,6b}$ 6.4, $J_{6a,6b}$ 11.4 Hz, H-6b), 4.22 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 3.96 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 1.1 Hz, H-4), 3.81 (ddd, 1 H, $J_{5,6a}$ 6.8, $J_{5,6b}$ 6.4, $J_{6a,6b}$ 11.4 Hz, H-5), 3.65 (dd, 1 H, $J_{1,2}$ 8.0, $J_{2,3}$ 10.6 Hz, H-2), 3.59 (s, 3 H, OMe), 3.55 (dd, 1 H, $J_{2,3}$ 10.6, $J_{3,4}$ 3.4 Hz, H-3).

Analysis: for $C_{14}H_{17}N_3O_6$ (323.3) Reported: C 52.01 H 5.30 N 13.00
Found: C 52.16 H 5.39 N 13.09

Methyl-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1→3)-O-[(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)]-6-O-acetyl-2-azido-2-desoxy-β-D-galactopyranoside (30)

Compounds 28 (100 mg, 0.3 mmol) and 19 (222 mg, 0.57 mmol) were dissolved in dichloromethane (6 mL); molecular sieves 4A (500 mg) were added and stirred at 20° for 1 hour. Then trimethylsilyltriflate (10 μL) was added and the mixture was stirred for another 8 hours at 20°. Additional trimethylsilyltriflate could be needed to bring the reaction to completion. Then the work-up was carried out as described for 22. 67

The reaction product 29 was dissolved in 1% methanolic sodium methoxide solution (5 mL); after 4 hours the solution was neutralized with AMBERLITE IRC-50 ion exchanger, filtered and concentrated down *in vacuo*. The acetylation was then carried out in absolute pyridine (4 mL) and acetic anhydride (1.0 mL) for 6 hours at 20°. The product was concentrated down *in vacuo* and purified by column chromatography on silica gel (ethyl acetate-petroleum ether 2:1, v/v); yield: 120 mg (51% relative to 28), syrup, $[\alpha]_D^{24}$ -32° (c 1.0, chloroform). ^{1}H-N.m.r. (400 MHz, $CDCl_3$): δ 5.39 (dd, 1 H, $J_{3',4'}$ 3.4, $J_{4',5'}$ 0.8 Hz, H-4'), 5.34 (dd, 1 H, $J_{3'',4''}$ 3.2, $J_{4'',5''}$ 0.6 Hz, H-4''), 5.20 (dd, 1 H, $J_{1'',2''}$ 8.0, $J_{2'',3''}$ 10.6 Hz, H-2''), 5.19 (dd, 1 H, $J_{1',2'}$ 7.8, $J_{2',3'}$ 10.4 Hz, H-2'), 5.03 (dd, 1 H, $J_{2'',3''}$ 10.6, $J_{3'',4''}$ 3.2 Hz, H-3''), 5.00 (dd, 1 H, $J_{2',3'}$ 10.4, $J_{3',4'}$ 3.4 Hz, H-3'), 4.98 (d, 1 H, $J_{1'',2''}$ 8.0 Hz, H-1''), 4.70 (d, 1 H, $J_{1',2'}$ 7.8 Hz, H-1'), 4.33 (dd, 1 H, $J_{2,3}$ 10.4, $J_{3,4}$ 3.4 Hz, H- 3), 4.09 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.06 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 0.6 Hz, H-4), 3.93 (m, 1 H, H-5''), 3.80 (m, 1 H, H-5'), 3.52 (s, 3 H, OMe), 3.35 (m, 1 H, H-5), 2.14, 2.11, 2.07, 2.06, 2.01, 2.01, 1.94, 1.92 (7 s, 27 H, 9 OAc).

Analysis: for $C_{37}H_{51}N_3O_{24}$ (921.8) Reported: C 48.21 H 5.58 N 4.56
Found: C 48.64 H 5.61 N 4.49

Benzyl-2-acetamido-3,6-di-O-benzyl-2-desoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-α-D-glycopyranoside (32)

Compounds[35] 31 (100 mg, 0.2 mmol) and 19 (74 mg, 0.19 mmol) were dissolved in dichloromethane (3 mL) and molecular sieves 4A (300 mg) added. After 1 hour at 20° trimethylsilyl triflate (0.2 mL) was added and the mixture stirred for 3 hours at 20°. The work-up was carried out as described for 22. The reaction product was purified by column chromatography (ethyl acetate-petroleum ether, 2:1, v/v); yield: 111 mg (71%); syrup, $[\alpha]_D^{20}$ +66° (c 1.0, chloroform). Crystals from ether-hexane (97 mg, 62%), melting point 108° $[\alpha]_D^{20}$ +64° (c o.7, chloroform); reference [28]: melting point 110-111° $[\alpha]_D^{20}$ +66° (c 1, chloroform); reference [29]: melting point 106-108° $[\alpha]_D^{20}$ +62° (c 0.55, chloroform).

^{1}H-N.m.r. (400 MHz, $CDCl_3$): δ 7.42–7.27 (m, 15 H, Ph), 5.28 (d, 1 H, $J_{NH,2}$ 9.2 Hz, NH), 5.24 (dd, 1 H, $J_{3',4'}$ 3.2, $J_{4',5'}$ 1.0 Hz, H-4'), 5.11 (dd, 1 H, $J_{1',2'}$ 8.2, $J_{2',3'}$ 10.4 Hz, H-2'), 4.93 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 4.79 (dd, 1 H, $J_{2,3}$ 10.0, $J_{3,4}$ 9.0 Hz, H-3), 4.65 (d, 1 H, $J_{1',2'}$ 8.2 Hz, H-1'), 4.23 (ddd, 1 H, $J_{5',6'a}$ 7.6, $J_{5',6'b}$ 6.2, $J_{6'a,6'b}$ 11.2 Hz, H-5'), 4.03 (dd, 1 H, $J_{3,4}$ 9.0, $J_{4,5}$ 9.8 Hz, H-4), 3.93 (dd, 1 H, $J_{5',6'a}$ 7.6, $J_{6'a,6'b}$ 11.2 Hz, H-6'a), 3.87 (dd, 1 H, $J_{5',6'b}$ 6.2, $J_{6'a,6'b}$ 11.2 Hz, H-6'b), 3.72 (dd, 1 H, $J_{5,6a}$ 3.2, $J_{6a,6b}$ 11.3 Hz, H-6a), 3.64 (dd, 1 H, $J_{3,4}$ 9.0, $J_{4,5}$ 9.8 Hz, H-4), 3.59 (dd, 1 H, $J_{5,6b}$ 1.8, $J_{6a,6b}$ 11.3 Hz, H-6b), 2.08, 1.97, 1.95, 1.79 (4 s, 12 H, 3 OAc und 1 NAc).

Analysis: for $C_{43}H_{51}NO_{15}$ (821.9) Reported: C 62.84 H 6.25 N 1.70
Found: C 62.90 H 6.41 N 1.71

Benzyl-2-acetamido-3,6-di-O-benzyl-2-desoxy-4-O-(3,4,6-tri-O-acetyl-2-desoxy-2-phthalimido-β-D-glycopyranosyl)-α-D-glycopyranoside (34)

Compounds[35] 31 (100 mg, 0.2 mmol) and 36 (reference [36]; 86 mg, 0.18 mmol) were reacted in dichloromethane (3 mL) in the presence of molecular sieves 4A (300 mg) and trimethylsilyltriflate (0.2 mL) at 20° as described for 32. The purification was carried out by column chromatography on silica gel (ethyl acetate - petroleum ether 1:1, v/v); yield: 91 mg (55%), syrup, $[\alpha]_D^{20}$ +55° (c 1.0, chloroform). 68

^{1}H-N.m.r.(400 MHz, $CDCl_3$):
δ 7.87–7.73 (m, 4 H, Phthaloyl), 7.37–7.15 (m, 15 H, Ph), 5.72 (dd, 1 H, $J_{2',3'}$ 10.6, $J_{3',4'}$ 9.0 Hz, H-3'), 5.49 (d, 1 H, $J_{1',2'}$ 8.4 Hz, H-1'), 5.19 (d, 1 H, $J_{NH,2}$ 8.4 Hz, NH), 5.11 (dd, 1 H, $J_{3',4'}$ 9.0, $J_{4',5'}$ 10.4 Hz, H-4'), 4.84 (d, 1 H, $J_{1,2}$ 2.8 Hz, H-1), 4.30 (dd, 1 H, $J_{1',2'}$ 8.4, $J_{2',3'}$ 10.6 Hz, H-2'), 4.15 (dd, 1 H, $J_{3,4}$ 9.4, $J_{4,5}$ 10.0 Hz, H-4), 4.13 (dd, 1 H, $J_{5',6'a}$ 4.0, $J_{6'a,6'b}$ 12.0 Hz, H-6'a), 3.87 (dd, 1 H, $J_{5',6'b}$ 1.0, $J_{6'a,6'b}$ 12.0 Hz, H-6b), 3.58 (ddd, 1 H, $J_{4',5'}$ 10.4, $J_{5',6'a}$ 4.0, $J_{5',6'b}$ 1.0 Hz, H-5'), 3.37 (m, 1 H, H-5), 2.02, 1.96, 1.80 (3 s, 12 H, 3 OAc und 1 NAc).

Analysis: for $C_{49}H_{53}N_2O_{15}$ (909.0) Reported: C 64.68 H 5.87 N 3.08
Found: C 64.92 H 6.01 N 3.12

Methyl-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-(1→4)-O-(2,3,6-tri-O-acetyl-β-D-galactopyranosyl)-(1→3)-2-azido-3,4-di-O-benzoyl-2-desoxy-β-D-galactopyranoside (35)

Compounds 11 (132 mg, 0.3 mmol) and 33 (170 mg, 0.25 mmol) were dissolved in dichloromethane(3 mL) then molecular sieves 4A (300 mg) and trimethylsilyltriflate (10 μL) were added. Additional trimethylsilyltriflate may be needed to bring the reaction to completion. After 6 hours at 20° the work-up was carried out as described for 22. Column chromatography was carried out on silica gel (ethyl acetate-petroleum ether 1:1, v/v); yield: 214 mg (66%), syrup, $[\alpha]_D^{24}$ -25° (c 0.2, chloroform).

1:1, v/v); Ausb. 214 mg (66%), Sirup, $[\alpha]_D^{24}$ −25° (*c* 0.2, Chloroform); ^{1}H-N.m.r. (400 MHz, $CDCl_3$): δ 8.05–7.42 (m, 10 H, Ph), 5.68 (dd, 1 H, $J_{3,4}$ 3.4, $J_{4,5}$ 0.8 Hz, H-4), 5.33 (dd, 1 H, $J_{3'',4''}$ 3.4, $J_{4'',5''}$ 0.8 Hz, H-4''), 5.14 (dd, 1 H, $J_{2',3'}$ 9.0, $J_{3',4'}$ 3.4 Hz, H-3'), 5.09 (dd, 1 H, $J_{1'',2''}$ 8.0, $J_{2'',3''}$ 10.8 Hz, H-2''), 4.95 (dd, 1 H, $J_{2'',3''}$ 10.8, $J_{3'',4''}$ 3.4 Hz, H-3''), 4.80 (dd, 1 H, $J_{1',2'}$ 7.6, $J_{2',3'}$ 9.0 Hz, H-2'), 4.49 (dd, 1 H, $J_{5,6a}$ 2.0, $J_{6a,6b}$ 12.0 Hz, H-6a), 4.43 (d, 1 H, $J_{1'',2''}$ 8.0 Hz, H-1''), 4.41 (dd, 1 H, $J_{5,6b}$ 7.0, $J_{6a,6b}$ 12.0 Hz, H-6b), 4.25 (d, 1 H, $J_{1',2'}$ 7.6 Hz, H-1'), 4.06 (d, 1 H, $J_{1,2}$ 7.2 Hz, H-1), 3.80 (dd, 1 H, $J_{3',4'}$ 9.0, $J_{4',5'}$ 9.6 Hz, H-4'), 3.64 (dd, 1 H, $J_{1,2}$ 7.2, $J_{2,3}$ 10.4 Hz, H-2), 3.57 (s, 3 H, OMe), 2.16, 2.12, 2.05, 2.01, 1.98, 1.95, 1.90 (7 s, 21 H, 7 OAc).

Analysis: for $C_{47}H_{55}N_3O_{24}$ (1045.9) Reported: C 53.97 H 5.30 N 4.02
Found: C 54.10 H 5.48 N 4.16

Methyl-2-azido-6-O-benzoyl-2-desoxy-3,4-di-O-trimethylsilyl-β-D-galactopyranoside* (?)**

Compound 28 (100 mg, 0.3 mmol) was dissolved in absolute dichloromethane (6 mL) and absolute pyridine (2 mL) then trimethylsilyltriflate (0.5 mL) was added. The product was concentrated down in vacuo and the residue was taken up in chloroform-water. The organic phase was dried out and then concentrated down in vacuo; yield: 116 mg (83%), syrup.

^{1}H-N.m.r. (400 MHz, $CDCl_3$): δ 8.05–7.31 (m, 4 H, Ph), 4.48 (dd, 1 H, $J_{5,6a}$ 6.6, $J_{6a,6b}$ 11.0 Hz, H-6a), 4.43 (dd, 1 H, $J_{5,6b}$ 6.4, $J_{6a,6b}$ 11.0 Hz, H-6b), 4.14 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 3.85 (dd, 1 H, $J_{3,4}$ 2.6, $J_{4,5}$ 0.6 Hz, H-4), 3.74 (ddd, 1 H, $J_{4,5}$ 0.6, $J_{5,6a}$ 6.6, $J_{5,6b}$ 6.4 Hz, H-5), 3.58 (s, 3 H, OMe), 3.56 (dd, 1 H, $J_{1,2}$ 8.0, $J_{2,3}$ 10.0 Hz, H-2), 3.42 (dd, 1 H, $J_{2,3}$ 10.0, $J_{3,4}$ 2.6 Hz, H-3), 0.19 (s, 9 H, Me_3Si), 0.13 (s, 9 H, Me_3Si).

Analysis: for $C_{20}H_{30}N_3O_6Si_2$ (464.4) Reported: C 51.58 H 6.52 N 0.90
Found: C 51.44 H 6.58 N 0.95

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* Translator's note: In the German text this reads "galactopynoside", but it certainly ought to be "galactopyranoside"

** Translator's note: The numerical reference for this compound is missing in the German text, but it apparently is not compound 36 since the structural formula for 36 given on page 9 of this translation is for a very different compound. This compound is also the only one for which the optical rotation data are missing.

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